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The Proof-of-Concept of Biochar Floating Cover Influence on Water pH

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Abstract

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Keywords

biochar, pH, water, buffering capacity, wastewater, highly alkaline porous biochar, gaseous emissions, colorimetric, visualization

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Article

The-Proof-of-Concept of Biochar Floating Cover Influence on Water pH

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Abstract: Studies have shown that biochar has the potential to remove organic and inorganic contaminants from wastewater. pH is known to have a crucial role in the transformation of pollutants. In this research, we explore the feasibility of using biochars properties to control the pH near the water–air interface, so the gaseous emissions from water (or wastewater) could be mitigated. This study aimed to test the effects of a thin layer biochar addition on the spatial and temporal variation of water pH. Two types of biochar and water were tested. Highly alkaline porous (HAP; pH 9.2) biochars made of corn stover and red oak (RO; pH 7.5) were applied surficially to tap (pH 9.5) and deionized water (DI) (pH 5.4). The spatial pH of solutions was measured every 1 mm of depth on days 0, 2, and 4 after biochar application. The results showed that HAP biochar increased the pH of both tap and DI water, while RO decreased tap water pH and increased DI water pH. On day 0, there was no effect on tap water pH, while a pH change in DI water was observed due to its lower buffer capacity. In addition, the pH (temporal) migration from topically applied biochar into an aqueous solution was visualized using a colorimetric pH indicator and corn starch to increase viscosity (to prevent biochars from sinking). The results prove that the surficial application of biochar to water was able to change both the pH near the water–air interface and the pH of the solution with time. The pH change was dependent on the biochar pH and water buffer capacity. These results warrant further research into the floatability of biochars and into designing biochars with specific pH, which could be a factor influencing gaseous emissions from liquids that are sensitive to pH.

Keywords: biochar; pH; water; buffering capacity; wastewater; highly alkaline porous biochar; gaseous emissions; colorimetric; visualization

1. Introduction

The increase in energy consumption, industrialization, and urbanization are having an impact on the environment that stems from wastewater discharged from agricultural, municipal, and industrial sources [1]. The United States Environmental Protection Agency (EPA) and the United States Geological Survey (USGS) examined treated and untreated water samples from approximately 25 different water treatment plants and reported ~250 microbiological and chemical contaminants [2]. A wide range of technologies is used for wastewater treatment, including biological treatment, chemical precipitation, phytoremediation, membrane removal, and ion exchange [3–5]. However, these treatments require significant operating, maintenance, and energy costs, and do not always show a sufficient removal of

contaminants [6]. Adsorbent materials are considered to be one of the possible wastewater treatment approaches and is especially applicable for organic compounds and heavy metals removal [7].

Biochar, a soil amendment, has shown great potential as an effective and low-cost adsorbent of contaminants from wastewater. Biochar is a solid carbonaceous by-product (char) obtained from pyrolysis, gasification, or torrefaction of biomass in low-oxygen conditions [8]. Sources of biochar include forestry and agricultural residues, animal manure, and sewage sludge [9]. Its properties vary due to the process temperature and duration and source of raw material. Typically, biochar is characterized by its ash content, pH, porosity, surface area, and C, H, O, N content [10,11]. Biochar has shown high removal capability of organic pollutants, and heavy metals from wastewater and pH of a solution had a significant impact on the removal rate. Table 1 shows the range of contaminants remediated from aqueous solutions by biochar.

Table 1. Relation of aqueous solution pH and biochar sorption.

Biochar Material	Scale of the Study	Objective of the Study	Biochar pH	Aqueous Solution pH	Solution pH after Biochar Application	Spatial pH Studied	pH Range
Anaerobic sludge digester [12]	laboratory	NH ₄ ⁺ removal from water	8.57–10.60	2–10	N/A	No	Adsorption significantly increased at solution pH 2–6
Maple wood biochar [13]	laboratory	NH ₄ ⁺ removal from aqueous solution	3.69–8.13	N/A	N/A	No	The greatest adsorption observed at pH 3.69 of biochar
Activated carbon [14]	laboratory	Phenols adsorption	3.4–10.4	2–12	N/A	No	Reduction decreased with increasing pH
Food waste [15]	laboratory	Phenol adsorption	6.40	3–11	N/A	No	Reduction decreased with increasing pH
Pinewood [16]	laboratory	Mg, Ca, Cr, and Pb adsorption	Not given	1–7	N/A	No	High sorption with increasing pH of the solution from 1 to 7
Magnetic Oak Bark Char Magnetic Oak Wood Char [17]	laboratory	Pb and Cd remediation	8.0 7.2	2–8	Initial pH raised after mixing with biochar for acidic solutions	No	The greatest sorption occurred at highest solution pH (8)
Mansonia wood sawdust [18]	laboratory	Cu and Pb removal from aqueous solution	6.71	2–6	N/A	No	The greatest sorption occurred at highest solution pH (6)
Pine woodchip Jarrah Activated carbon [19]	laboratory	Cu and Zn removal	7.79 9.43 9.93	2–6	Initial solution pH increased after biochars application	No	Removal rate increases with increasing solution pH. Activated carbon > Jarrah > Pine woodchip

Several hypotheses regarding the mechanism of how sorption capacity of biochar related to pH of the solution have been proposed. Moreno-Castilla et al. stated that adsorption of weak phenol compounds on carbonaceous char surface depended on the degree of dissociation of the compounds and charge on the surface of the char and both processes were related to pH of the aqueous solution [18]. According to Niazy et al., the highest sorption of As(III) was observed in the 3–7 pH range, while removal decreased at pH from 8–10 [19]. Abdel-Fattah claimed that the highest sorption occurred at pH 6–7 for Mg(II), Ca(II), and Pb(II), while Cr(VI) had maximum adsorption at pH 1 [20]. All these studies showed the importance of pH on the efficiency and mechanism of the removal of pollutants from aqueous solutions. To date, the majority of research has been focused on biochar-aided sorption in aqueous solutions. However, biochar properties (e.g., low density) could be also exploited to mitigate emissions of pH-sensitive pollutants to the air.

The objective of this study was to test the effects of biochar addition on the spatial (changing with depth) and temporal (changing with time) distribution of water pH (Figure 1). The surficial application of biochar (~6 mm thick layer) was used for its techno-economic feasibility of scaling up to mitigation of gaseous emissions from large area sources. Two types of biochar and water were tested. Highly alkaline porous (HAP; pH 9.2) biochars made of corn stover and red oak (RO; pH 7.5) were applied surficially to tap (pH 9.5) and deionized water (DI) (pH 5.4). Because this experiment included not the only diffusion of OH⁻ ions from biochar, but also the convection during measurements, the colorimetric method, using pH indicator was used to visualize changes in pH distribution with time and depth.

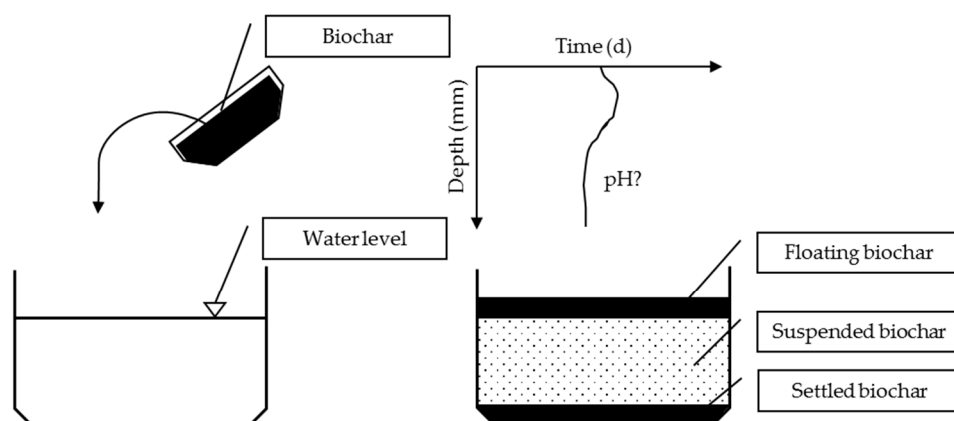


Figure 1. The objective of this study—the study of the spatial and temporal distribution of pH due to surficially applied biochar to water.

2. Materials and Methods

2.1. Biochar Properties

Highly alkaline and porous (HAP) biochar made of corn stover and red oak (RO) biochar were used. 5 g of biochar was added to 25 mL of DI water then pH was measured after 3 h of equilibration. To measure pH at a zero-point charge (ZPC), the solids addition method was used, where the initial pH of 1M NaCl solution was changed from pH 2 to 11 by addition of 1M HCl and 1M NaOH. After adding 0.1 g of biochar into each solution and shaking them for 24 h, the final pH of every solution was measured. Difference between initial and final pH against initial pH was plotted and the intersection of resulting curve and initial pH was ZPC [21].

A C/N combustion analyzer was used to determine elemental content (C, H, N, and S) of biochars [22]. Biochar properties such as moisture content, volatile matter, fixed carbon, and ash content were measured according to method Rover et al. [23]. Properties of HAP and RO biochars are shown in Table 2, below:

Table 2. Properties of HAP and RO biochars used in the experiment.

Properties	HAP	RO
pH	9.2	7.5
Zero-point charge	8.42	6.75
C (%)	61.37	78.53
H (%)	2.88	2.54
N (%)	1.21	0.62
S (%)	0.07	0.02
Moisture (%)	1.93	3.03
Volatile matter (%)	16.27	26.38
Fixed carbon (%)	34.98	54.76
Ash (%)	46.82	15.83

Fourier transform infrared (FTIR) analysis was used to examine the biochars samples for functional groups. The sample was scanned 32 times at a resolution of 4 cm^{-1} on a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) with attached Smart iTR accessory, with a wavenumber range of $750\text{--}4000\text{ cm}^{-1}$. The results of the FTIR analysis are shown elsewhere [24].

Pore images of biochars were taken using scanning electron microscopy (SEM) (FEI Quanta 250 FE-SEM). Samples were attached to carbon adhesive disks and coated with iridium to improve imaging of the samples.

2.2. Water

The properties of the tap water that was used for the experiment are given in Table 3:

Table 3. Properties of the tap and DI water used in the experiment [25].

Properties	Tap	DI
pH	9.2	5.4
Chlorine residual (ppm)	2.82	0

Note: Additional properties are listed in Tables A1 and A2 (Appendix A).

2.3. Bromothymol Blue Solution (BTB)

BTB solution was prepared as a pH indicator which would visualize pH change of tap and DI water. BTB ACS reagent (Acros Organics, Morris Plains, NJ, USA) was used to prepare a BTB solution. Corn starch (Argo, Oakbrook Terrace, IL, USA) was used to increase the viscosity of the BTB solution, and sulfuric acid with 36 Normality was used to adjust its pH to 6.

2.4. Experiments

The research was divided into two experiments:

- The determination of biochar type influence on spatial and temporal distribution of pH in tap and DI water;
- The visualization of pH change from different types of biochar in controlled solutions.

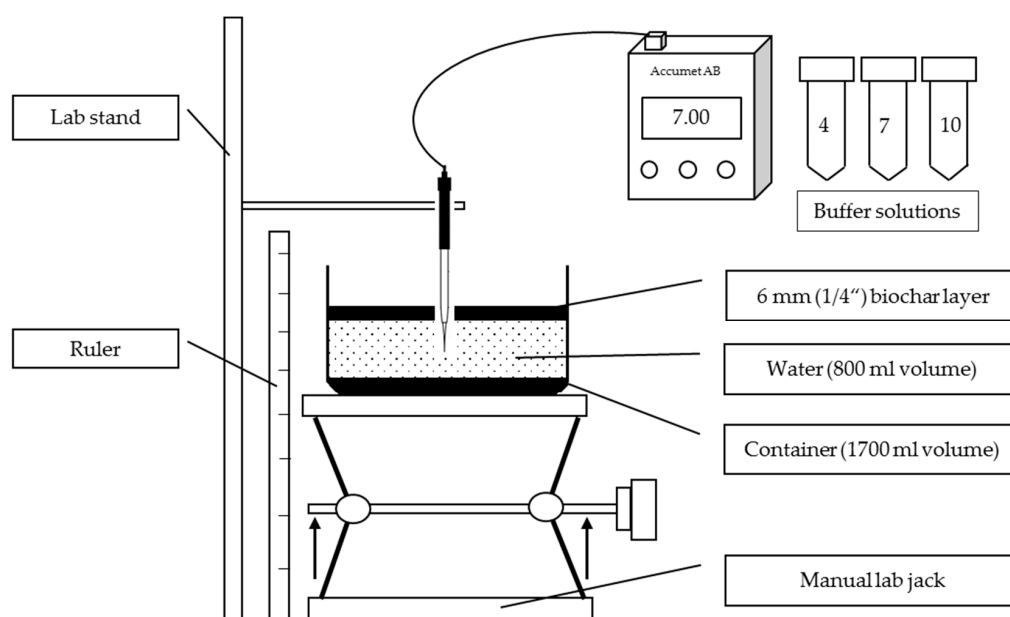
2.5. The Determination of Biochar Type Influence on Spatial and Temporal pH of Tap and Deionized Water

Three glass containers for food storage with a volume of 1700 mL (dimensions $19\text{ cm} \times 14.5\text{ cm} \times 7.5\text{ cm}$) were filled with 800 mL of tap water and another three filled with 800 mL of DI water. The HAP and RO biochars were superficially applied on two of the triplicated treatments, and remaining triplicate was a control. The matrix of the experiment is presented in Table 4.

Table 4. The matrix of the experiment.

Treatment	Water Used	
RO biochar	Tap	Deionized
HAP biochar	Tap	Deionized
Control (no biochar)	Tap	Deionized

A thin pH microelectrode (MI-415 Series Micro-Combination pH Probe, Microelectrodes, Bedford, NH, USA) [26], connected to an Accumet AB 15 pH meter [27], was calibrated with 4, 7, 10 pH buffer solutions and attached to a laboratory stand. A manual lab jack, with a container on the top of it, was placed under the pH probe, and the jack was elevated in increments of 1 mm using a ruler placed next to it. After the probe had penetrated the water to the depth of 3.5 cm, pH measurements were collected every 1 mm of the depth. The pH probe was rinsed and wiped before taking measurements from the next container. 6.35-mm-thick (~1/4 inch) layers of HAP and RO biochar with weights of 48 g and 58 g, respectively, were applied on Day 0, and measurements were taken for each container on Days 0, 2 and 4. The experimental stand is presented in Figure 2. The selection of biochar dose (thickness) was driven by our previous experience with thin biochar layers with swine manure for the control of gaseous emissions [28].

**Figure 2.** Experimental design for testing biochar influence on spatial pH distribution in water.

Tap and DI water were titrated to identify their buffer capacity. 0.1 M of sulfuric acid was prepared by adding 5.611 mL of stock solution in 1000 mL of DI water, and 5.281 mL of concentrated NaOH was added to prepare a 0.1 M solution. A drop of sulfuric acid and NaOH was added in tap water and DI water respectively using graduated burette and pH was measured after each drop.

2.6. The Visualization of pH Change from Different Types of Biochar Diffusion in Controlled Solutions

To visualize the influence of two types of biochar on pH change in a controlled solution, a separate experiment was carried out with a colorimetric pH indicator. BTB was used as a pH indicator. The pH indicator solution was prepared according to the following procedure [29]:

- 1) 0.1 g of BTB powder was mixed with 10 mL of a 4% solution of sodium hydroxide;
- 2) 20 mL of 99.9% of methanol was added;
- 3) The solution was diluted in 1 L of DI water.

BTB changed color according to its pH. After mixing 25 mL of BTB solution and 75 mL of tap and DI water, respectively, the solutions were 'deep blue' at pH 11.4 and then poured into a 200 mL bottle. The pH-controlled solution was prepared according to the following procedure:

- 1) To acidify the BTB solution, a solution of 20 μL sulfuric (VI) acid (H_2SO_4) in 25 mL of tap water was added, drop by drop, until the pH of the BTB solution dropped to 6 and the color turned to 'light yellow'. The pH was read using the thin pH probe connected to pH meter.
- 2) To prevent random biochar sinking in the BTB solution and the effects of convection, 5 g of corn starch was added and mixed while heated at the temperature of 80 $^{\circ}\text{C}$. This process increased the viscosity.
- 3) After complete dissolution of starch, the prepared mixture was poured to 3 glass bottles with 200 mL of volume. Bottles were filled in half and kept in room temperature for cooling and increase of viscosity.
- 4) HAP and RO biochars were applied to the top of the two solutions, and the third one was a control. Biochars were applied surficially with a thickness of 10 mm.


For inhibition of biological decomposition of starch, bottles with pH-controlled solutions and biochars were kept in the refrigerator under 4 $^{\circ}\text{C}$ during the 4 days of the experiment. Each day, bottles were taken out from the refrigerator, and photos showing the changes of pH were taken. Photos were taken using a smartphone with the following specifications: dual camera: (1) 16 MP, f/1.7, 27 mm (wide), 1/2.8", 1.12 μm , PDAF; (2) 20 MP, f/1.7, 27 mm (wide), 1/2.8", 1.0 μm , AF, PDAF.

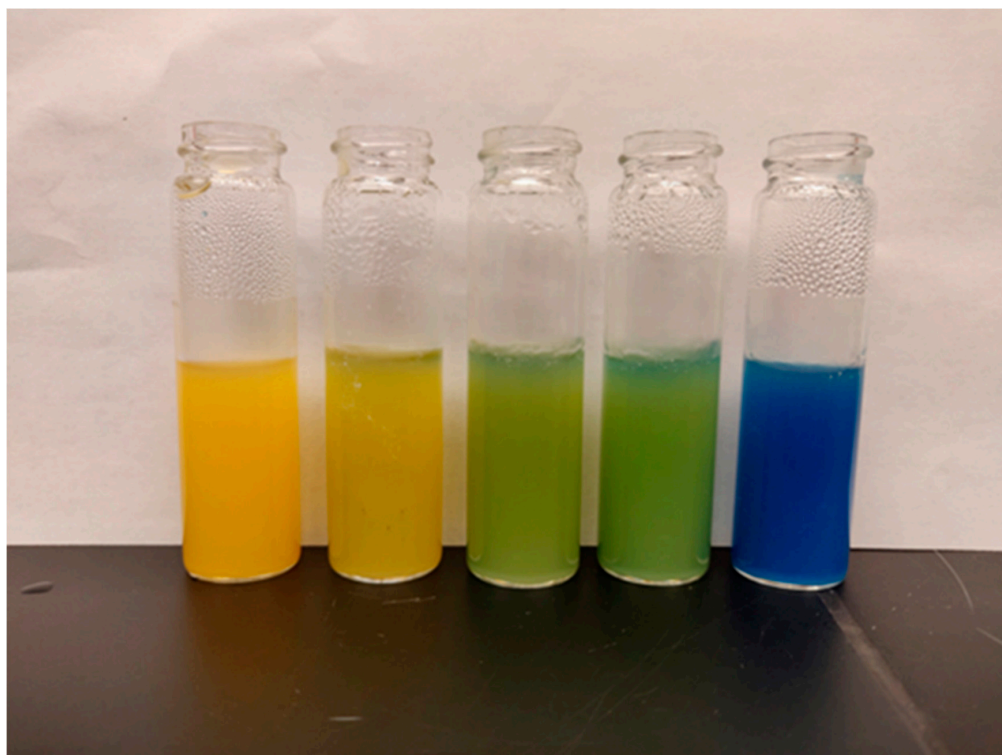
To correlate BTB color with its pH, 5 mL of BTB solutions were prepared at pH < 4.6, 6.05, 6.60, 7.05, 8.5 (Figure 3), following the above-mentioned procedure. The mobile application "Color Grab" [30] was used to measure L^*A^*B values of color results were presented in Table 5. After addition of 0.1 g of corn starch into each BTB solution at different pH, the colors became brighter (Figure 4), and new color values were showed in Table 6. The color of pH indicator changes to yellow-green-blue when pH is acidic-neutral-alkaline, respectively.




Figure 3. Range of colors of BTB solution in water at marked pH conditions.

Table 5. L*A*B values of BTB solutions at different pH.

pH	L	A	B	Color
<4.6	57.6	19.8	63.7	
6.05	55.3	−26.9	58.6	
6.60	19.9	−22.3	7.2	
7.05	9.9	4.6	−22.0	
8.5	28.9	25.3	−56.3	

**Figure 4.** Different colors of bromothymol blue at marked pH conditions after adding corn starch.**Table 6.** L*A*B values of BTB solutions at different pH after adding starch.

pH	L	A	B	Color
<4.6	53.0	5.6	57.4	
6.05	42.4	−9.2	12.7	
6.60	43.1	−14.5	43.5	
7.05	41.6	−18.0	33.5	
8.5	22.6	11.4	−38.5	

2.7. Statistical Analysis

A simple linear regression model was used in the R program (R i386 3.6.0. Ink) to analyze the data and estimate p -value. A level of significance of 0.05 was used to determine statistical significance.

3. Results

3.1. The Determination of Biochar Type Influence on Spatial and Temporal pH of Tap and Deionized Water

After application, HAP biochar sank immediately, and on day 3, most of the biochar particles had settled on the bottom of the container for both tap and DI water. However, there was still a thin floating layer of biochar close to the water surface and suspended particles floating in the water. Contrariwise, most of the RO biochar was floating on the top of the tap and DI water surface. The top of the biochar layer remained dry until day 4, while the lower wet part of the layer that interacted with the water expanded (Figure 5). Figures 6 and 7 document how HAP and RO biochars sank after days 0, 2, and 4, with red boxes indicating biochar floating on the surface of the water and green and blue boxes illustrating the suspended and settled fractions of biochar, respectively.

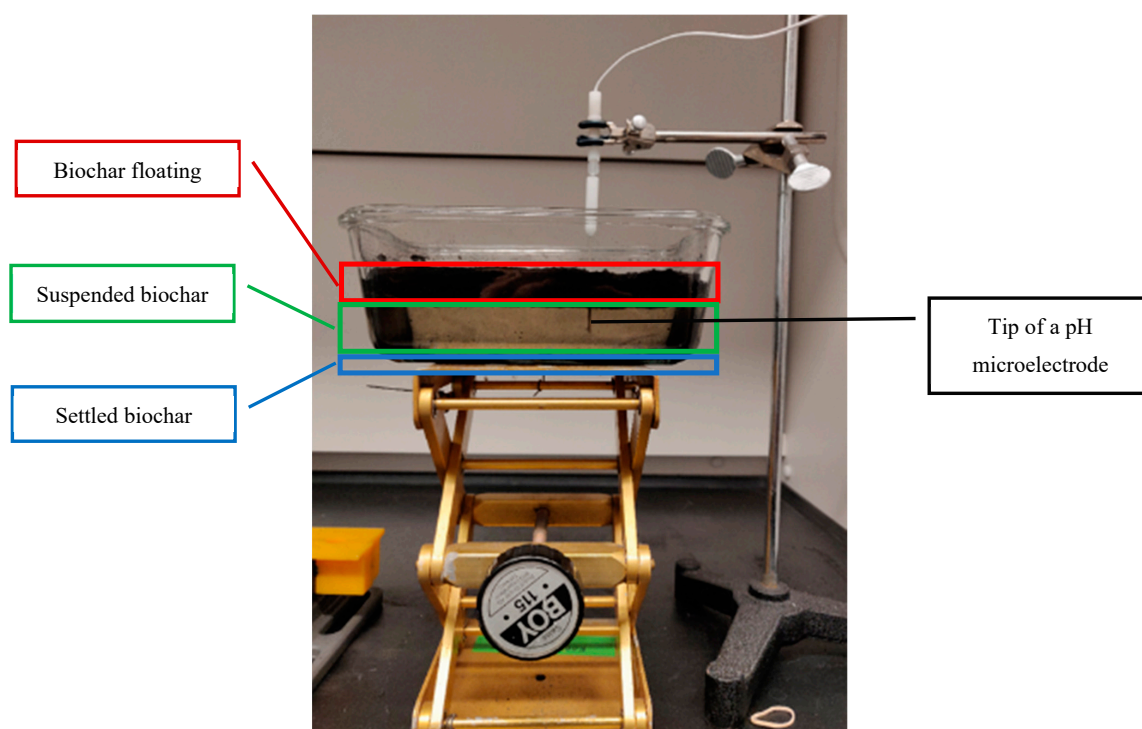


Figure 5. Process of taking pH measurements of tap water with floating RO biochar.

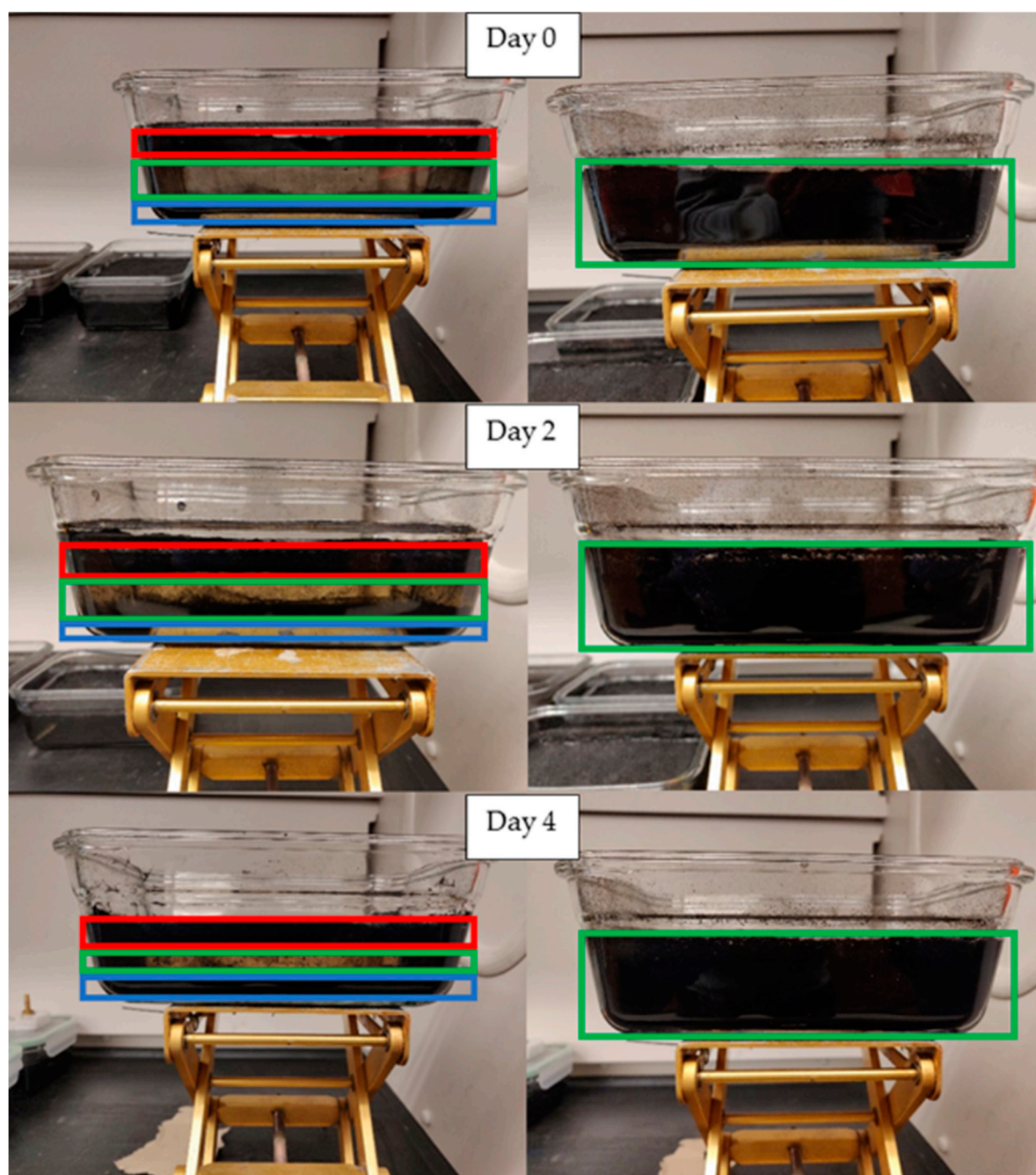


Figure 6. Photos of RO (left) and HAP (right) biochars applied on DI water on days 0, 2, and 4. Frames show biochar behavior (red—floating, green—suspended, blue—settled biochar).

According to Figure 8, on day 0, HAP biochar had significant ($p < 0.0001$) influence on tap water pH one hour after application. There was significant ($p < 0.0001$) difference in pH between tap water control and HAP biochar treated water after 2 days where pH increased from 8.3 to 9.2; then, pH dropped to 8.9 ($p < 0.0001$) on day 4. However, HAP biochar had a significant ($p < 0.0001$) effect on DI water and raised its pH from 5.4 to 9.5 ($p < 0.0001$) 1 h after application, and it stayed approximately the same until day 4.



Figure 7. Photos of RO (left) and HAP (right) biochars applied on tap water on days 0, 2, and 4.

The same trend was observed with RO biochar, which had a significant effect ($p < 0.0001$) on the pH of tap water on day 0. However, the pH of tap water decreased on day 2 from 8 to 7.8 ($p < 0.0001$) and stayed the same until day 4. RO biochar raised the pH of DI water from 5.4 to 6.7 ($p < 0.0001$) and 7 ($p < 0.0001$) on days 2 and 4, respectively (Note: additional interpretation of treatments effect by days is presented in Figure A1, Appendix A).

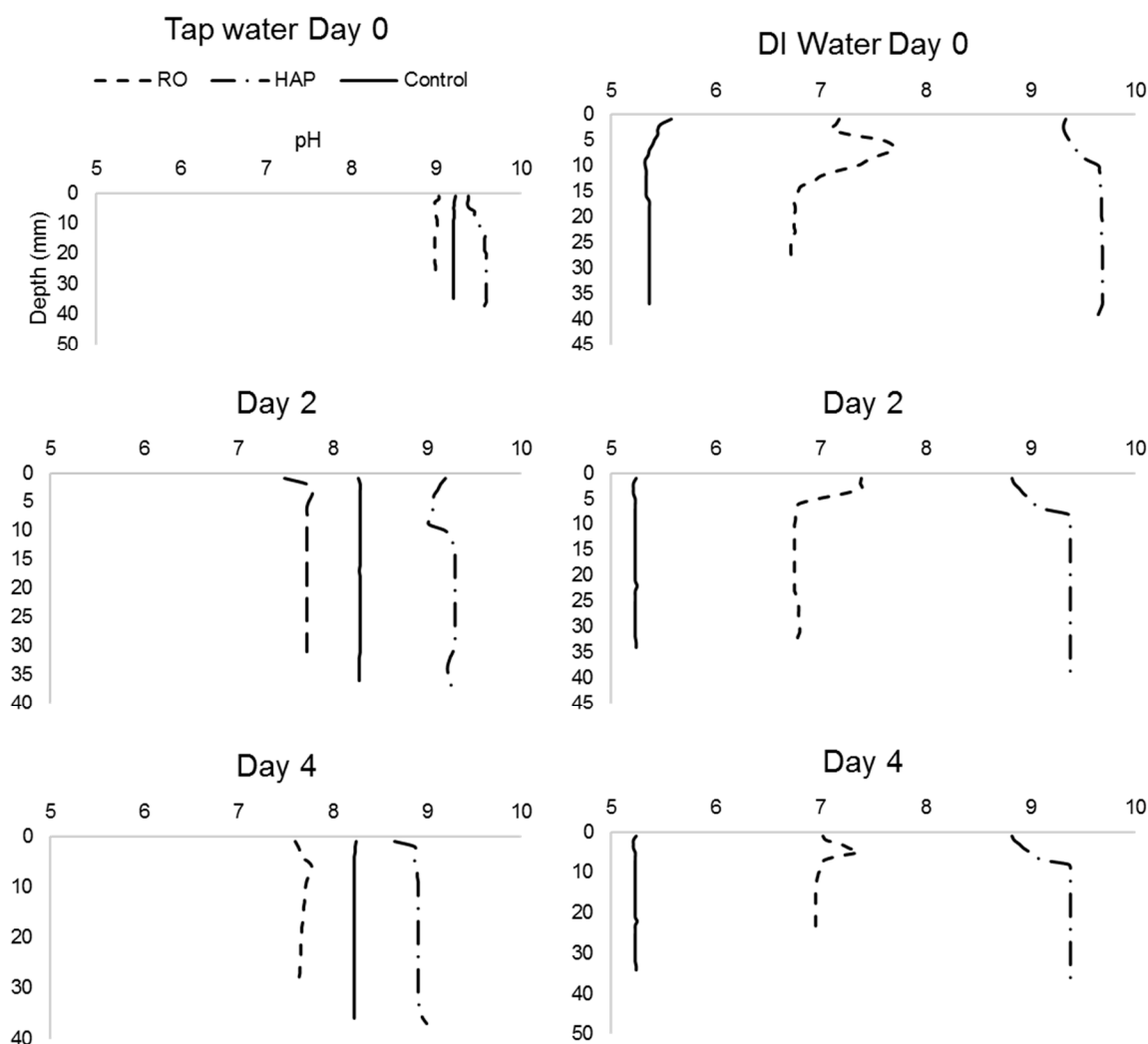


Figure 8. pH distribution in tap and DI water due to RO and HAP biochars in comparison with control. Additional information is provided in Table A2.

3.2. The Visualization of pH Change from Different Types of Biochar Diffusion in Controlled Solutions

On day 0 and ~2 h after HAP biochar application on tap water/BTB/starch solution, the pH indicator changed its color from yellow (pH 6) to blue (pH 8.5 and higher) due to the high alkalinity of the HAP biochar, and the thickness of the blue portion of the solution was ~4 mm. The influence of the HAP biochar increased over the following days, and the blue color thickened to 10, 12, and 19 mm on days 2, 3 and 4, respectively. The influence of RO biochar on tap water/BTB/starch solution was also observed (Figure 9).

HAP biochar had the same influence trend on DI water/BTB/starch solution, with blue color thicknesses of 4, 10, 13, and 19 mm on days 1, 2, 3, and 4, respectively. The influence of RO biochar on the solution could be observed on days 3 and 4 with a color change from yellow (pH 6) to light green (pH 6.6–7.05). The thickness of green color due to the influence of RO biochar was 3 and 6 mm on days 3 and 4, respectively (Figure 10).

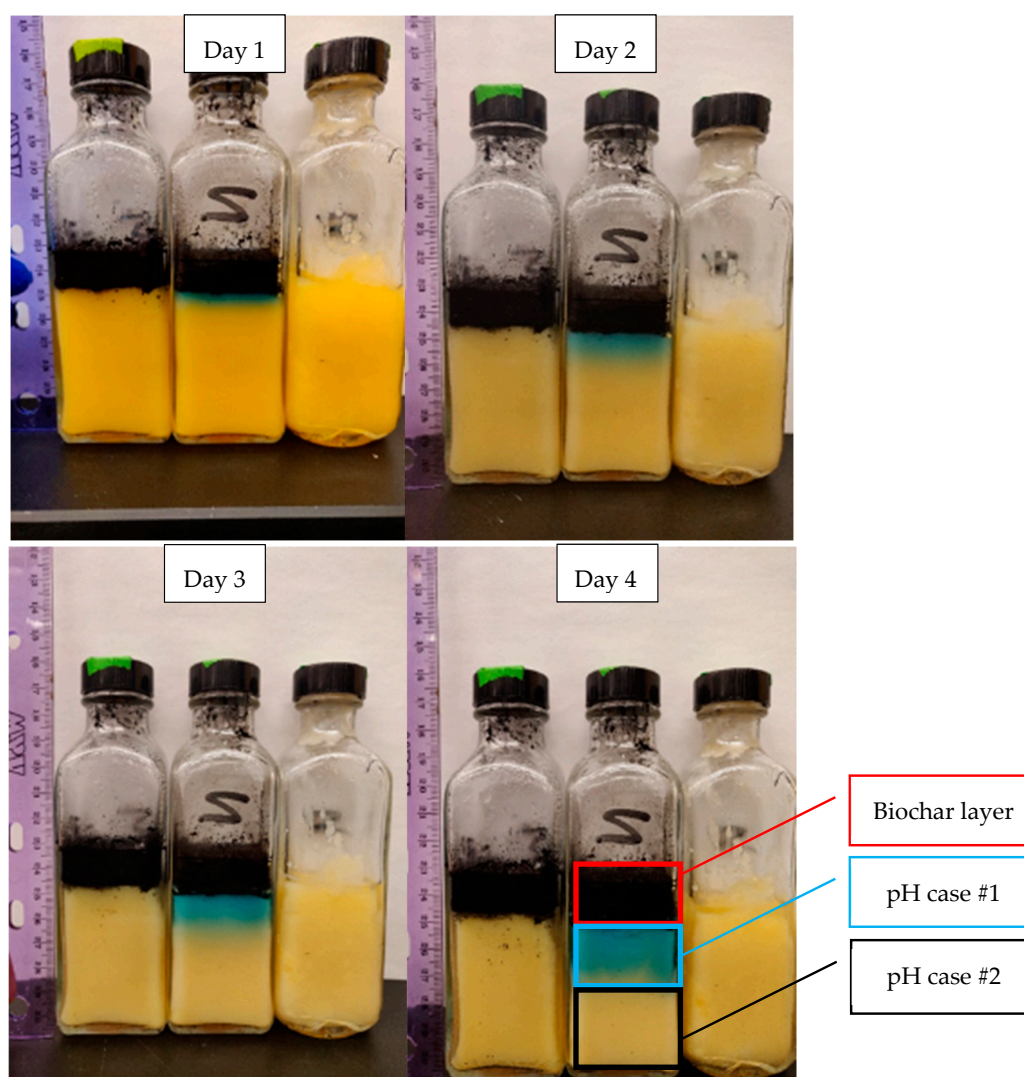


Figure 9. Visualization of pH change from different types of biochar in a controlled solution. RO biochar on top of tap water/BTB/starch solution on the left; HAP biochar on the middle changes pH indicator color from yellow to dark green; control solution on the right.

Colorimetric L*A*B values for both solutions were analyzed by “Color grab” application and are shown in Tables 7 and 8.

Table 7. L*A*B values for color changes of tap water/BTB/starch solution due to HAP biochar influence on day 4.

pH	L	A	B	Color
Case #1	40.3	−18.1	−4.4	
Case #2	62.2	3.7	45.7	

Table 8. L*A*B values for color changes of DI/BTB/starch solution due to HAP biochar influence on day 4.

pH	L	A	B	Color
Case #5	47.4	−3.8	30.1	
Case #3	43.6	−20.4	6.9	
Case #4	66.7	3.1	49.2	

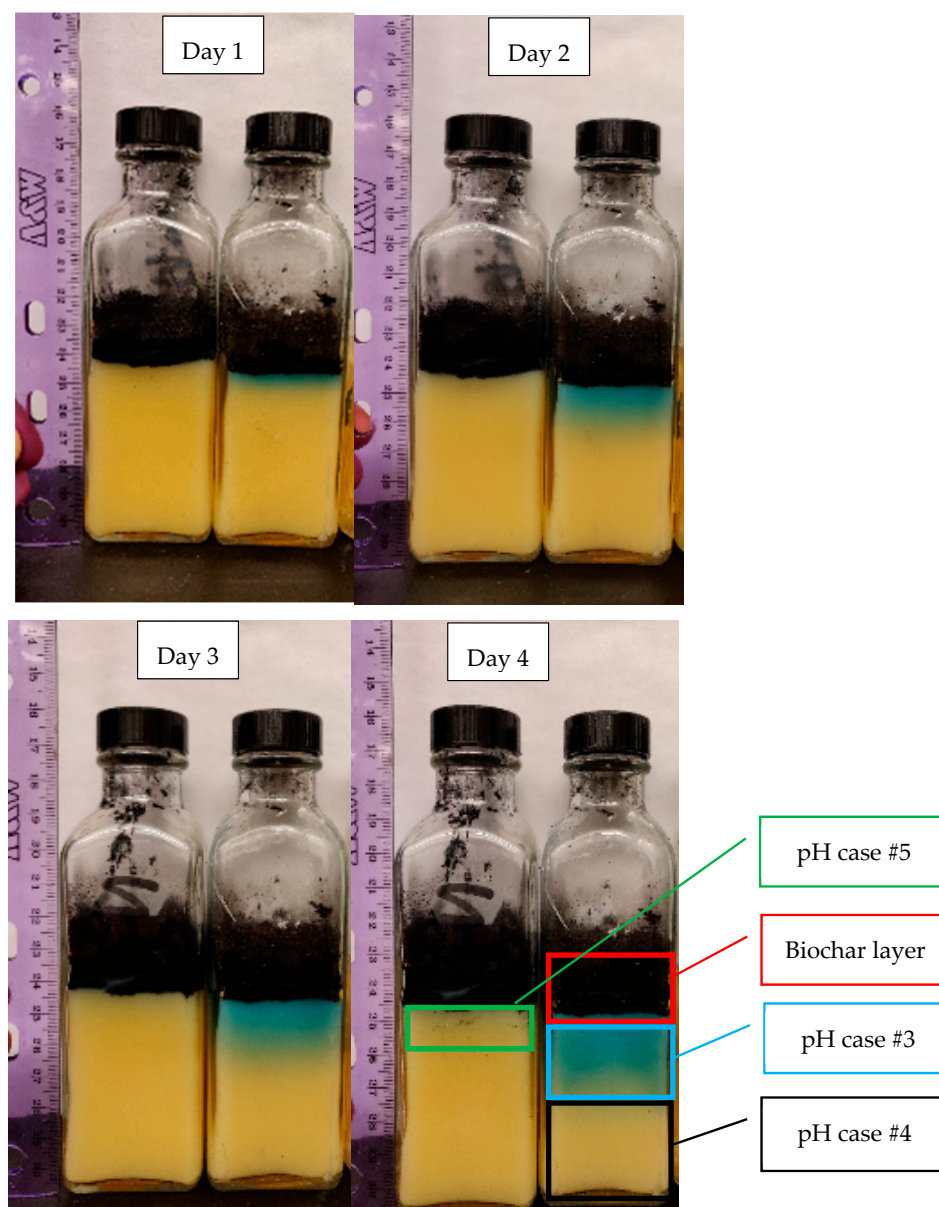


Figure 10. Visualization of pH change from different types of biochar in a controlled solution. RO biochar on top of DI water/BTB/starch solution on the left changes pH indicator color from yellow to light green (pH 7); HAP biochar on the middle changes pH indicator color from yellow to dark green.

4. Discussion

4.1. The Determination of Biochar Type Influence on Spatial and Temporal pH of Tap and Deionized Water

Both biochars had less effect on tap water on day 0, while water pH changed due to the influence of HAP and RO biochars on days 2 and 4 (Figure 10). DI water changed its pH from 5.4 to ~9.4 and 7 due to HAP and RO treatments, respectively, on day 0 and had no apparent change after that. The reason for the immediate effect of biochars on DI water pH was low buffer capacity of DI water in comparison with tap water (Figure 11).

The larger pores of HAP biochar could also be the reason for its sinking in both types of water, whereby water easily penetrates into the HAP biochar pores and makes it sink, while RO, with smaller pores, floats on the top of tap and DI water (Figure 12).

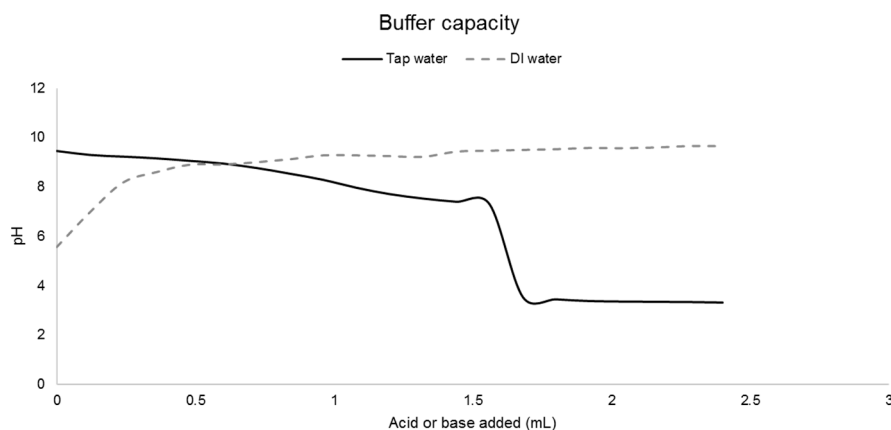


Figure 11. Buffer capacity of tap and DI water.

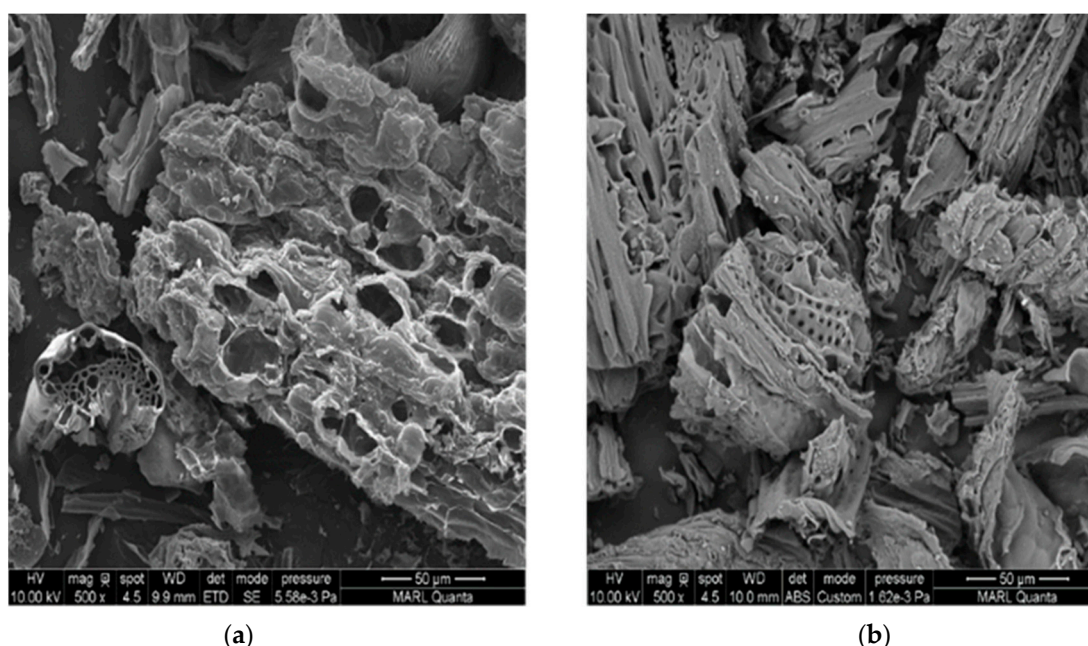


Figure 12. SEM results showing and pores of HAP (a) and RO (b).

This experiment opened promising approaches to treating wastewater or manure stored in animal housing by amending the pH at the air–liquid interface. This could open up research to mitigate hazardous and odorous compounds emissions by using biochar as a topically applied bio-cover that is able to influence pH. As was shown in Figures 6 and 7, biochar with properties close to RO used in this experiment (which was floating on the water surface), would be most suitable as the bio-cover.

Further study will be testing the effect of topically applied biochar on spatial and temporal change of pH of swine manure. According to Mroz, manure acidification is able to inhibit NH_4^+ transformation into NH_3 [31]. Biochar floating on top of manure, could potentially change manure pH (which could lead to a reduction of ammonia emissions) and capture volatile compounds due to its porous matrix.

Surficial application of a powdery substance like biochar to large areas of water or wastewater could be problematic. This is due to the potential hazards linked with self-ignition, and practical issues related to the storage and transportation of biochar. A potential solution could be the pelletization of biochar [32,33], which greatly densifies the biochar and reduces the potential of hazardous gas emissions from the biochar itself. Pelletized biochar could be easier to apply using existing technology. However, the floatability and gradual dissolution of pellets to create a floating cover on the water–air interface warrants further research.

4.2. The Visualization of pH Change from Different Types of Biochar Diffusion in Controlled Solutions

The buffer capacity of the water was also a key parameter in the experiment of visualization of pH migration. The pH of tap water/BTB/corn starch solution was not affected due to RO biochar and retained the same color for 4 days. However, DI/BTB/corn starch solution pH changed with the RO biochar and turned light green on day 3 due to the lower buffer capacity of DI water in comparison with tap water. Corn starch, which was used to increase viscosity the solution, could slow down pH migration, where it took several days to change the solution pH for biochars, while they had a fast influence on clean water pH. The innovation of this experiment was in using corn starch, which increased the viscosity of the aqueous solutions without changing their pH. Starch could be applied to make aqueous solutions with increased viscosity without affecting its properties needed to visualize pH changes.

5. Conclusions

This research opens promising approaches for treating wastewater or animal manure by amending the pH in the air–liquid interface. The results of controlled experiments showed that HAP biochar increased pH of both tap and DI water pH, while RO decreased tap water pH and increased DI water pH. On day 0, there was no effect on tap water pH, while a pH change in DI water was observed due to its lower buffer capacity. In addition, the pH (temporal) migration from topically applied biochar into an aqueous solution was visualized using a colorimetric pH indicator and corn starch to increase viscosity. The results prove that the surficial application of biochar to water was able to change both the pH near the water–air interface and the pH of the solution with time. The pH change depended on the biochar pH and water buffer capacity. The result warrants further research of floatability of biochars and designing biochars with specific pH, which could be a factor influencing gaseous emissions from liquids that are sensitive to pH.

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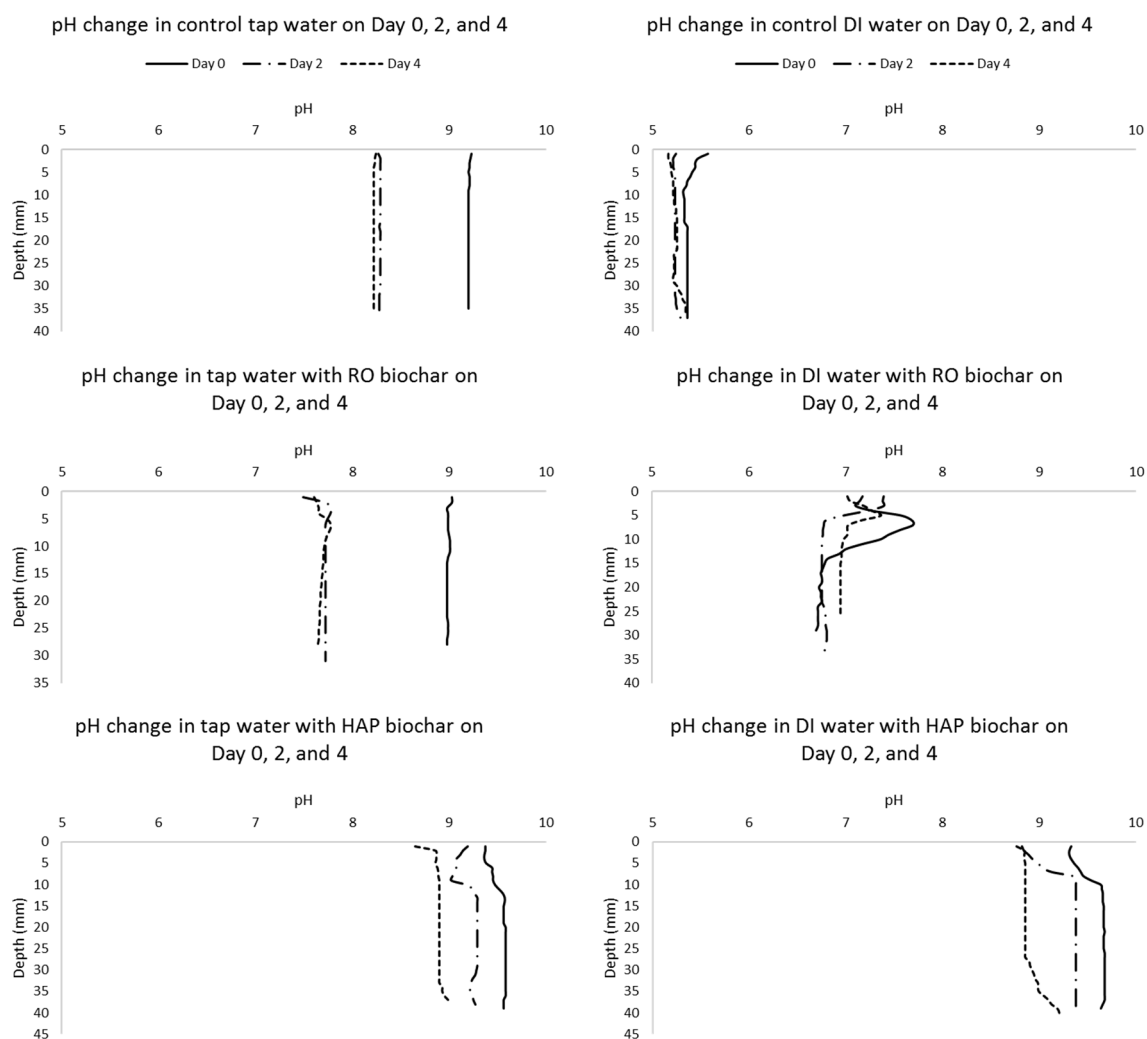
Appendix A

Table A1. Properties of tap water used in the experiment.

Treated Water Quality	Value
Non-carbonate hardness, ppm	123
Total hardness, ppm	174
Total hardness, grains per liter	2.7
Fluoride content, ppm	0.68
Iron content, ppm	0.02

Table A2. Water purification system specifications for DI water.

Carbon filter	
Chlorine removal	0 ppm at carbon effluent
Organics removal	Natural occurring, large molecular weight
Ultraviolet light-1	
Purpose	Bacterial reduction
Water quality	High purity water
Wavelength	254 nm
Dosage	30,000 microwatt s cm ⁻² after 9000 h
Microbacterial (<i>E-coli</i>) reduction	99.9%
Ultraviolet light-2	
Purpose	Bacterial reduction
Water quality	High purity water
Wavelength	254 nm
Dosage	30,000 microwatt s cm ⁻² after 9000 h
Microbacterial (<i>E-coli</i>) reduction	99.9%

**Figure A1.** pH distribution in tap and DI water due to RO and HAP biochars in comparison with control.

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